



Full Length Article

Graphene oxide/polyurethane-based solid–solid phase change materials with enhanced mechanical properties



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ABSTRACT

Graphene oxide (GO) crosslinked polyurethane-based solid–solid phase change materials, composed by polyethylene glycol (PEG) and hexamethylene diisocyanate biuret (HDIB), were fabricated in-situ polymerization. GO sheets could support the excellent solid framework at 100 °C and prevent the leakage of melt in synergy with HDIB by physical and chemical crosslinking network. Meanwhile, GO sheets act as heterogeneous nucleation agents that make the crystallization temperature of system rise to 34.0 °C from 24.8 °C with 14.5 wt% GO. Whereas, GO have little effect on the latent heat, which may be an offset of the nucleation and confinement. Besides, the tensile strength increased to 21.7 from 10.2 MPa with 14.5 wt% GO and Young's modulus increased to 471.5 from 180.1 MPa for 44.6 wt% one. Also, the strain at break has a slight promotion within 14.5 wt% GO. The synthesized system would be potential to be applied in thermal energy storage fields.

1. Introduction

In recent decades, the perceived risks of increased gap between energy supply and demand, conventional fossil fuels depletion and their pollution to environment all urge the exploitation of renewable energy [1–3]. Phase change materials (PCMs) with high latent heat capacity are particular appealing for thermal and solar energy storage applications, which could absorb and store the excess energy that would otherwise be wasted, and then release heat when the conditions are suitable for phase transition [2,4–6]. It shows great potential for PCMs to reduce the consumption of fossil fuels that would inevitably discharge lots of pollutants, and at the same time, improve the energy efficiency [7,8].

PCMs can be generalized into three main types, solid-gas, solid-liquid and solid–solid PCMs, according to phase transition process. Most commonly used PCMs are solid-liquid ones, including paraffin wax, polyethylene glycol (PEG), fatty acids and salt hydrates [5]. PEG, has drawn tremendous interests to researchers due to its incomparable advantages such as suitable phase change temperature, nontoxic, non-corrosive, good biocompatibility, chemically stability as well as low-cost [9,10]. Leakage during phase transition is the main drawback that severely hampers their applications [11]. Therefore, numerous measures, containing physical and chemical means, have been taken to solve this thorny problem.

One facile strategy is vacuum impregnation, in which PEG is infiltrated into porous matrix like hydroxyapatite [12], mesoporous silica [13], metal organic frameworks [14] and aerogels [15]. However, the weak physical interaction between PEG and porous matrix always leads to poorly recycling reliability. Comparatively, chemical bonding can readily guarantee the long-lasting solid–solid stability until the degradation of materials. Thus, grafting or blocking PEG onto other skeleton such as poly(styrene-co-maleic anhydride) [16], polystyrene [17] and isocyanates [18–25] is an effective approach. Among these, fabrication polyurethane-based solid–solid phase change materials (PUSSPCMs) has gathered considerable attentions in recent years for numerous merits including easily being processed, no additional containers, no gas or liquid generation and so on [22,23]. PEG, serving as soft phase change part, is blocked into hard segments composed of diisocyanates and chain extenders. The chemical bonding and physical forces like hydrogen bonds are responsible for keeping the solid framework.

Graphene oxide (GO), derived from graphene, is a monolayer-structured material with abundant oxygen-containing groups like carboxyl, hydroxyl and epoxide, which facilitate the modification of GO and make it a promising nanofiller for versatile applications [26–29]. Also the hydroxyl groups could react with isocyanates to form covalent urethane bonds between polyurethane (PU) matrix and GO sheets, which does favor to the homogeneous dispersion of GO and

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reinforcement of interfacial compatibility [30–32]. Cai et al. [30] obtained the enhanced PU with Young's modulus that is 7 times higher than the pure PU just incorporating 4 wt% GO. Shamis et al. [31] improved the Young's modulus of PU through in-situ polymerization to 12.08 fold. The covalent bonding between GO and PU imparts better compatibility and maximizes the enhancement effect.

Generally, most researchers ignore the mechanical properties when settling the leakage problem. In this paper, we fabricated a series of PUSSPCMs by in-situ polymerization. Here, GO sheets were reacted with isocyanate to consolidate the supporting skeleton based on hexamethylene diisocyanate biuret (HDIB) through constructing a double network both physical and chemical crosslinking, which endows the system with excellent form-stability and no trace of any leakage during phase change process. At the same time, the good dispersion of GO can give the greatest effect in enhancing the matrix. The mechanical properties of the system had got dramatic enhancement, which is of great significance for the practical applications. The materials hold great promise for a range of applications like solar energy storage, smart textile etc.

2. Experimental

2.1. Materials

Graphite flakes (300 mesh), potassium permanganate (KMnO_4) and polyethylene glycol (PEG, $M_n = 4000$) were all purchased by Sinopharm Chemical Reagent Co., Ltd., Beijing, China. And PEG was dried under vacuum at 110°C for 3 h before use. Sulfuric acid (H_2SO_4 , 98%), hydrochloric acid (HCl, 37%), phosphoric acid (H_3PO_4 , $\geq 85\%$), hydrogen peroxide (H_2O_2 , 30%) and *N,N*-Dimethylformamide (DMF) were obtained from Beijing Chemical Works, China. DMF was distilled under vacuum after refluxed and stirred overnight. Hexamethylene Diisocyanate Biuret (HDIB, N75, with $\text{NCO}\% = 15.6\%$, which was gotten by "di-*n*-butylamine-toluene" method, the structure is given in Fig. S1 in supporting information) was purchased from Bayer (Germany) and used as received.

2.2. Synthesis of GO sheets

GO was synthesized from graphite by a modified Hummer's method [34,35]. Briefly, 1 g graphite flakes and 6 g KMnO_4 were mixed uniformly with stirring into a three-neck round bottomed flask. Then, the mixture of H_2SO_4 and H_3PO_4 (120 ml:13.3 ml) was added slowly into the flask under continuously stirring in ice bath. After, the flask was moved to oil bath at 50°C and stirred for 12 h. The result mixture was then slowly poured into 133 ml frozen deionized water. The H_2O_2 was added dropwise into the mixture until the color turned into golden yellow. Then, 133 ml 5% HCl solution was poured into the above mixture. Finally, the crude product was rinsed repeatedly with deionized water by centrifuge until the pH was neutral. The final product was dried at 50°C for use.

2.3. Preparation of GO/PUSSPCMs

GO/PU-SSPCMs, named GPCM-*x*, where *x* is number of the sample, was synthesized in-situ polymerization, and the synthetic route is shown in Scheme 1. First, the calculated GO powder was dispersed into DMF with the assistance of cell disrupter. Then, the DMF solution of PEG was ultrasonically mixed with GO dispersion. The result mixture was then moved into the oil bath at 60°C and HDIB was added subsequently. The synthesis process was conducted for 1 h under the protection of nitrogen. Soon afterwards, the solution was poured into petri-dishes and curing at 60°C for 24 h to get the final GPCM-*x*. Table 1 lists the formulation of the products.

2.4. Characterization

The structure and surface morphology of GPCM-*x* and GO nanosheets were characterized with Vertex 70 Fourier transform infrared spectrometer (FTIR, Bruker, Germany) over the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$, Thermo ESCALAB 250 X-ray photoelectron spectroscopy (XPS) using Al-K α radiation, and XL-30 field emission scanning electron microscopy (SEM) with an acceleration voltage of 10 KV, respectively.

The phase transition properties were measured by X-ray diffraction (XRD), polarized optical microscopy (POM) and differential scanning calorimeter (DSC). The crystalline morphology of GPCM-*x* was obtained visually by POM (Leica DM2500P, Germany) equipped with a Linkam hot stage (UK). XRD measurements were performed at room temperature using Bruker D8 Advance (Germany) with Cu K α radiation ($\lambda = 0.154\text{ nm}$). The scans were conducted in the range of diffraction angle $2\theta = 5 - 45^\circ$. DSC (TA Q20, USA) was employed to characterize the melting and crystallization temperature and the latent heats of GPCM-*x* under nitrogen flow. First, the sample was heated to 100°C at a rate of $30^\circ\text{C}/\text{min}$ and isothermal for 3 min to eliminate the thermal history. Then, the sample was cooled to 0°C and heated again to 100°C at a rate of $10^\circ\text{C}/\text{min}$.

The thermal stability of samples was assessed by Thermogravimetric analysis (TGA, Mettler Toledo, Switzerland). The tests were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 800°C in a nitrogen stream.

The thermal reliability was conducted by accelerated thermal cycling test using. To better characterize the thermal reliability of the system, all the samples in Aluminium pan, which were tested by DSC, were placed in the furnace of a high-low temperature chamber and suffered 499 consecutive heating and cooling process, in which the temperature was altered between 10 and 100°C and each cycle was completed by 20 min with a respective 3 min isothermal at 10 and 100°C . The whole test process took a week. After that, the samples were tested again by DSC.

The mechanical properties were evaluated at room temperature using Instron 5869 universal testing machine according to Chinese standard method (GB/T 1040. 1–2006).

3. Results and discussions

3.1. Structural and morphological characterization of GPCM-*x*

The construction of crosslinking network in GPCM-*x* lies greatly on the reaction activity of isocyanate with hydroxyl, which could be reflected by FT-IR spectra of GO, PEG and GPCM-*x*, as shown in Fig. 1. The FT-IR spectrum of GO shows characteristic absorption peaks at 3224 , 1720 , 1624 , 1219 and 1040 cm^{-1} , which correspond to $-\text{OH}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$ in aromatic, $-\text{COO}-$, $\text{C}-\text{O}-\text{C}$ of epoxide stretching vibration, respectively. To further determine the chemical composition of GO, XPS measurement was conducted. The C1s spectra of GO were fitted and the results are shown in Fig. 1(b). The C1s spectrum of GO contains four components of nonoxygenated carbon at 284.6 eV , carbon in $\text{C}-\text{OH}$ at 286.1 eV , $\text{C}-\text{O}$ at 286.8 eV and $\text{C}=\text{O}$ at 288.4 eV . The calculated content of $\text{C}-\text{OH}$ is about 20.4%. The characteristic absorption peaks of PEG at 3458 and 1108 cm^{-1} belong to the $-\text{OH}$ stretching vibration and $\text{C}-\text{O}-\text{C}$ symmetrical vibration, respectively, and the absorption peaks of $\text{C}-\text{H}$ bonds appear at 2888 , 1468 , 962 and 842 cm^{-1} . A new absorption peak of 1715 cm^{-1} , which is attributed to the stretching vibration of $-\text{NHCOO}-$, emerges in GPCM-*x*, indicating the successfully synthesis of polyurethane. The spectrum of GPCM-3 is identical with GPCM-0 because there is no other new groups generating except $-\text{NHCOO}-$ and $\text{NH}-\text{CO}-\text{C}-$, although GO sheets participated in the reaction.

The prepared GO are wrinkled sheets with an average size of $12\text{--}15\text{ }\mu\text{m}$ (Fig. S2). The morphologies of fracture surface of GPCM-*x*

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